A SIMPLE PROCEDURE OF SEMI-QUANTITATIVE SPECTRAL ANALYSIS OF CALCIUM, STRONTIUM, BARIUM AND LITHIUM.

By Kunizô HUKUDA.

Received December 25, 1926. Published May 28, 1927.

In the course of a research on the permeability of the frog-skin, it occurred to me to analyse very dilute solutions of alkali and alkali-earth metals. In this case, I applied the spectral analysis introducing some improvements in its practical procedure, which enabled me to perform the semi-quantitative analysis, and the results thus obtained were accurate enough for the purpose of biochemical studies. On account of the simplicity of the method, which may be carried out even in a laboratory not equipped with modern spectroscopical instruments, I believe, it is worth describing.

Apparatus Employed. An induction coil which can discharge through the maximum spark gap of 3.5 cm. is connected to a fulgurator, the positive pole of which comes from the bottom of the vessel containing the solution to be tested, and its point protrudes slightly above the liquid surface. The distance between the poles is adjusted to be 1–2 mm., whichever gives the best result. In the primary circuit of the induction coil stands a battery, as well as a reversing key (Fig. 1).

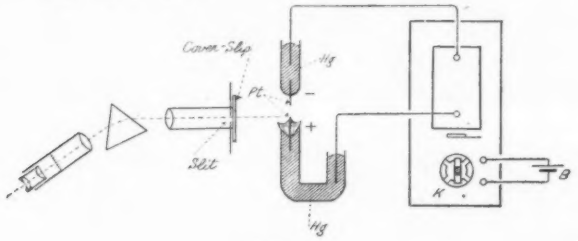
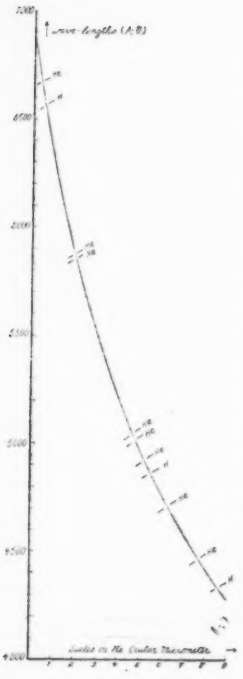


Fig. 1.

By this arrangement, in which the poles are reversed[1] to the usually adopted system, the spark is highly luminous at the anode and the spectral

(1) This process differs from the well-known "procédé du spectre de renversement" after Lecoq de Boisbaudran in the respect, that in that classical method the solution itself serves as the anode, and it is the luminesced part of the solution that is observed spectroscopically.



F ig. 2.

lines thus observed, in directing carefully the collimator of the spectroscope towards the point of the anode, are quite specific to the metal in the solution, accompanied by a number of non-specific lines. The spectroscope employed was an ordinary prism spectroscope of low dispersion, D_1 and D_2 lines of sodium being just possibly resolved.

The Determination of the Wave-lengths. As the standards of the wave-lengths of spectral lines, some neon-, helium- and hydrogen- lines were used; these spectral lines of known wave-lengths[1] were observed through an eye-piece provided with an ocular micrometer on its focal plane, in adjusting the direction of the telescope such that the yellow line of neon (5852.4 Å) comes just upon the scale division 2.00 (Fig. 2), and a curve which represents the relation between the wave-lengths (ordinates) and the micrometer scales (abscissae) was drawn. By the aid of the ocular micrometer and this reference curve, the wave-length of any unknown line is easily determined approximately.

As we are dealing with the spark spectrum across air between the platinum electrodes, it is expected that the lines due to air and platinum present themselves constantly as non-specific lines. Care must be taken, therefore, not to confuse them with those to be identified in the practise of analysis. The most marked of them are,

Colour	λ observed.	λ identified.[2]	Probable source
Green	5685	5686, -80	N
Green	5008	5001, -05,-07,-11	N
Blue	4862	4854	Pt
Blue	4712	4705, -10	O(?)
Blue	4660	4662	O(?)
Blue	4650	{4642, -51 {4643, -55	O(?) N
Blue	4484	4478	N

(1) Baly, "Spectroscopy." 3rd ed., Vol. I, p. 126 (1924).
(2) Kayser, "Tabelle der Hauptlinien der Linienspectra aller Elemente," (1926).

Furthermore, in the fulgurator filled with a solution, there always appears a red line, $\lambda=6563$ due to hydrogen, even when filled with distilled water; and it is also quite difficult to suppress the appearance of the D-doublet lines, because of their very high sensibility.

For the determination of wave-lengths of those spectral lines that are situated in the red to yellow region, another simple method is applicable. The fulgurator, namely, is put close in front of the slit of the collimator, which is protected by a micro cover-slip from being soiled; and a neon lamp ("Glimlamp") stands behind the fulgurator. By such an arrangement any metallic line in this region, which is to be identified, may be found between two neon lines with known wave-lengths. We estimate by interpolation how far the line in question is located from one of the neon lines, say that having a shorter wave-length, and we can thus easily calculate the approximate wave-length of the metallic line.

In relation to this it may be worth remarking here that the "Glimlamp" gives 21 neon lines to the left of the yellow line ($\lambda=5852.4$)[1] inclusive, two of which—the one $\lambda=5364.9$ and the other probably composed of $\lambda=5606.4$ and $\lambda=5602.4$ but fused together owing to the low resolving power of our apparatus—are not found listed in some current text-books, while the line $\lambda=7032.4$ was not visible to the author.

Identification of the Specific Lines. By either of the two methods above mentioned, the wave-lengths of spectral lines of several metals produced by our reversed pole procedure are determined and thus identified, taking the Kayser's table[2] or Eder and Valenta's atlas[3] as reference. The results are given below:

LiCl, 1/750 M. Two lines are to be observed: an orange line is found between two neon lines, $\lambda=6143$ and $\lambda=6096$, while a red line is situated just resolvably close to the neon line $\lambda=6717$. Thus the estimated and identified wave-lengths of these red and orange lines are as follows:

Colour	λ estim.	λ ident.
Red	6712	6708
Orange	6101	6104

LiCl, 0.11 M. In this case also two and no more lines came to sight. They are, as identified by the reference curve,

(1) Baly, loc. cit., p. 37 (1924).
(2) Kayser, loc. cit.
(3) Eder u. Valenta, "Atlas typischer Spectren," (1911).

Colour	λ estim.	λ ident.
Red	6715	6708
Orange	6100	6104

KCl, 1/750 M. No lines characteristic to this metal were observed, although persisting lines are expected at $\lambda=4047$ and $\lambda=4044$.

RbCl, 1/750 M. and *CsCl*, 1/750 M. In both cases, no specific lines bright enough to be utilised for our purpose, were detected.

$MgCl_2$, 1/750 M. Three lines of greenish blue colour were observed. They are so highly characteristic in their arrangement that we can recognise them at the first glance. The determination of their wave-lengths gave the following results.

Colour	λ estim.	λ ident.
Greenish blue	5177	5184
„	5170	5173
„	5166	5167

$BaCl_2$, 1/750 M. The following six lines were observed:

Colour and intensity	Position compared with Ne-lines
Red	Almost superposing on the line 6506.5
Bright orange	„ 6143.0
Pale yellow	„ 5852.4
Brilliant green	——
Brilliant blue	——
Brilliant indigo	——

Besides these lines, no bands were detected. The character of the barium spectrum obtained by this method shows thus more resemblance to its spark spectrum than to the flame spectrum.

$BaCl_2$, 0.09 M. In this concentration, barium chloride solution, if in a favourable condition, gives a number of distinct lines, the wave-lengths of which were determined as follows:

Colour	λ estim.	λ ident.
Red	6595	6595
"	6505	6499,-97
Orange	6137	6142
Striated in the orange region	6105	6111
	6060	6063
	6007	6019
	5993	5997
	5965	5972
Striated in the yellow region	5848	5854
	5828	5826
	5779	5778
Green	5537	5536
Blue	4935	4934
"	4920	4900,-03 (?)
Indigo	4556	4554

$SrCl_2$, 1/750 M. In this dilution, only few lines and bands were observed, namely two (sometimes more) weak green lines, two or more blue lines and one intense indigo line. Besides these lines, a striated red band and a distinct narrow orange band were visible.

$SrCl_2$, 0.1 M. The following numerous lines and bands were observed:

Colour and character	λ estim.	λ ident.
Red band	6880–6770	Band No. 1.
" "	6745–6640	" No. 2.
" "	6630–6555	" No. 3.
Red line	6460	6464,-56
Red band	6460–6420	Band No. 4.
Red line	6350	6346
Red band	6350–6310	Band No. 5.
Red line	6240	6229
Red band	6240–6207	Band No. 6.
" "	6105–6015	Band No. 7.
Orange-red line	6055	6059
Orange band	5975–5936	5970,-5940
Green line	5537	5543
" "	5518	5522
" "	5503	5504
" "	5476	5481
Blue line	5259	5259
" "	5237	5239
" "	5226	5230,-22
" "	4956	4962
" "	4871	4876,-72
" "	4831	4832
" "	4813	4812
" "	4793	4784
" "	4747	4742
" "	4723	4722
Indigo line	4612	4608
Violet line	—	4306
" "	—	4216

$CaCl_2$, 1/750 M. The following lines and bands were detectable:

Colour and character	Intensity
Orange-red line	Very weak, often invisible when the lamp is lighted.
Green line Red to orange band Narrow green band	Quite intense.

$CaCl_2$, 0.1 M. The wave-lengths of the following lines and bands were determined:

Colour and character	λ estim.	λ ident.
Red band	6525–6363	
Intense red band	6310–6157	
Lines in the intense red band	6250 6202 6180	6265 6202 6180
Orange line	5938	5933
Orange band	6155–5890	
Green band	5576–5493	
Lines in the green band	5559 5520	5543 5517

Accuracy and Limit of Application of this Method. In order that this spectroscopical method may be utilised for the semi-quantitative analysis of certain metals from salt solutions, its accuracy should be determined beforehand with solutions containing the salts in various known dilutions. And it is recommended to list the results in reference tables characterising the arrangement and apparatus made use of by each worker. In the author's own case, it proved as shown in the following tables, in which the degrees of brightness of the lines and bands are marked with − (invisible), ± (hardly visible), + (visible), ++ (bright) and +++ (brilliant). The results obtained with lithium, barium, strontium and calcium were satisfactory:

Colour and wave-length	Relative concentration (1 = 1/750 M.)					
	0.025	0.05	0.1	0.25	0.5	1
Lithium chloride:						
Red, 6708	−	±	+	+	++	++
Orange, 6104	−	−	±	+	+	++
Barium chloride:						
Red, 6499–7	−	−	−	−	+	+
Orange, 6142	−	−	±	+	+	++
Yellow, 5854	−	−	−	−	−	+
Green, 5536	−	−	+	+	++	+++
Blue, 4934	−	−	+	+	++	+++
Violet, 4554	−	−	−	−	+	++
Strontium chloride:						
Red bands	−	−	±	+	+	++
Orange band	−	−	−	±	+	++
Green lines	−	−	−	−	±	±
Blue lines	−	−	−	−	±	±
Indigo, 4608	−	−	±	+	++	+++
Violet, 4306	−	−	−	+	++	+++
Violet, 4216	−	−	−	+	++	+++

Colour and wave-length	Relative concentration (1 = 1/750 M.)					
	0.025	0.05	0.1	0.25	0.5	1
Calcium chloride:						
Intense red band	−	−	−	+	+	++
Orange band	−	−	±	+	+	++
Green band	−	−	−	±	+	+

The probable limits of detection of Ca, Sr and Ba by this method, calculated in terms of mg. of the metals in 1 c.c. of solution and compared with those of Bunsen's classical method as well as of Riesenfeld and Pützer's process, are shown below:

	Bunsen's flame analysis.	Riesenfeld & Pützer.	Present author.
Ca	0.2 mg in 1 c.c.	0.002	0.013
Sr	0.6 "	0.03	0.029
Ba	14 "	0.006	0.018
Li	—	—	0.0009

According to the description of Riesenfeld and Pfützer,[1] their method, which is often quoted as a process representing the highest sensibility attainable by the spectral analysis, requires at least about 1 c.c. of the solution to be tested, while in the present procedure, only 0.1 c.c. or even a smaller quantity of solution is sufficient to carry out one test, owing to the small capacity of the fulgurator-vessel.

Summary.

1. A simple procedure of the semi-quantitative spectral analysis has been described.

2. This procedure consists in observing salt solutions fulgurated in a special fulgurator, with the electrodes reversed, i. e. the anode in the solution.

3. Accuracy and limit of application of this method were carefully studied and it was found that this is especially suited for the analysis of minute quantities of lithium, calcium, strontium and barium.

In carrying out this study, the author owes much to the suggestion and encouragement of Prof. Hashida and Prof. Nagai, as well as to the kind interest and care taken by Prof. Y. Shibata of the Faculty of Science of this University. Sincere thanks are also expressed here to the friendship of Dr. Shinki of the Military Institute for Scientific Research.

Physiological Institute, Faculty of Medicine,
Tokyo Imperial University.

(1) Riesenfeld and Pfützer, *Ber.*, 46 (1913), 3140.

DAS SPEZIFISCHE GEWICHT WÄSSRIGER BLAUSÄURE.

Von **Manjiro SHIRADO.**

Eingegangen am 15. Februar 1927. Ausgegeben am 28. Mai 1927.

Das spezifische Gewicht wässriger Blausäure von 1 bis 16% HCN bei 15.56°C. hat bereits Ure[1] gemessen, kürzlich haben Walker und Marvin[2] eine interessante und mühevolle Arbeit veröffentlicht, weiter haben Gay-Lussac[3], Bleekrode[4], Meyer-Hopf[5] und Enklaar[6] das spezifische Gewicht reiner Blausäure gemessen. Aber das spezifische Gewicht von 0 bis 100 %-ige Blausäure bei bestimmter Temperatur ist noch unbekannt. Wir mussten das spezifische Gewicht wässriger Blausäure messen.

Die wässriger und wasserfreier Blausäure aus chemische reines Ferrocyankalium und Phosphorsäure dargestellt (vgl. M. Shirado, diese Zeitschrift, 2 (1927), 85).

Das spezifische Gewicht wässriger Blausäure haben wir mit einem Kugelförmigen Pyknometer[7] gemessen; sein Inhalt ist ca. 25 c.c. Die zu messende Lösung wurde ungefähr 10–15 Minuten in den Thermostaten von 18.0°C. gehängt, dann in das Pyknometer mittels Pipette möglichst schnell eingefüllt und der eingeschliffene Stopfen, der ein Thermometer trug, eingesteckt. Das Pyknometer stand dabei in einem Gefäss, das mit Wasser von 18.0°C. gefüllt war. In diesem Gefäss wurde das Pyknometer in das Wägezimmer getragen, gut getrocknet und schnell gewogen. Die Messung 100 %-iger Blausäure bei 18.0°C. war äusserst schwer; entweder kamen einigen Blasen in den Hals des Pyknometers oder einige Tropfen der Blausäure spritzten aus dem Kapillarrohr heraus, da ja der Siedepunkt reiner Blausäure bei 25.7°C. liegt. Aber nach einiger Erfahrung konnten diese Schwierigkeiten überwunden werden durch möglichst schnelles Füllen und schnelles Abwiegen.

Folgende Tabelle enthält die Ergebnisse der Messung. Fig. 1. zeigt die Abhängigkeit des spez. Gewichtes von der Konzentration.

(1) „Chemiker Kalender," II, S. 275 (1926).
(2) M. Walker und C.J. Marvin, *Ind. Eng. Chem.*, 18 (1926), 139.
(3) Gay-Lussac, *Ann. chim.*, [1] 95 (1815), 145.
(4) Bleekrode, *Jahresbericht über die Fortschritte der Chemie*, 1884, S. 284.
(5) K.H. Meyer und H. Hopf, *Ber.*, 54 (1921), 1712.
(6) C.J. Enklaar, *Rec. trav. chim.*, 42 (1923), 1006.
(7) Vergl. Stähler, „Handbuch d. Arbeitsmethoden" III (1), S. 40, Fig. 6, Form 3.

Tabelle 1.

Spezifisches Gewicht wässriger Blausäure[1] bei 18.0°C.

Gewichtsprozent	Spez. Gewicht $\left(\frac{18°}{18°}\right)$	Spez. Gewicht $\left(\frac{18°}{4°}\right)$	
		In der Luft.	Reduzierte Werte auf den leeren Raum.
5.052 %	0.9927	0.9914	0.9914
9.770	0.9841	0.9827	0.9828
10.04	0.9838	0.9824	0.9825
14.58	0.9732	0.9718	0.9719
19.70	0.9593	0.9579	0.9580
20.29	0.9578	0.9565	0.9565
26.90	0.9376	0.9363	0.9364
33.01	0.9167	0.9154	0.9155
39.26	0.8987	0.8975	0.8976
46.01	0.8757	0.8745	0.8747
47.68	0.8658	0.8646	0.8648
52.00	0.8518	0.8506	0.8508
55.37	0.8428	0.8416	0.8418
60.23	0.8290	0.8279	0.8281
60.76	0.8270	0.8259	0.8261
69.50	0.7953	0.7942	0.7945
70.93	0.7925	0.7914	0.7917
79.54	0.7598	0.7587	0.7590
80.18	0.7582	0.7572	0.7574
88.55	0.7289	0.7279	0.7282
89.64	0.7265	0.7255	0.7258
100.00	0.6919	0.6909	0.6913

Zwischen 27 % und 100 % HCN-Gehalt ist die Abhängigkeit des spezifische Gewichts von der Konzentration annähernd linear; unterhalb 27 % biegt die Kurve merklich ab.

Die Punkte, die Walker und Marvin bei 18°C. gefunden haben, liegen alle genau auf der von uns gefundenen Kurve (siehe Fig. 1). Das spezifische Gewicht reiner Blausäure hat Gay-Lussac bei 18°C. zu 0.6969 gefunden, während wir bei 18.0°C. in der Luft $D^{18.0}_{18.0} = 0.6919$ und $D^{18.0}_{4} = 0.6909$ ge-

(1) Die Blausäure enthielt zwecks Conservierung eine Spur Phosphorsäure. Eine Überschlagsrechnung ergab, dass die zugesetzte wässrige Phosphorsäure (spez. Gew., 1.7) bei 100 % Blausäure den 1/1220 Teil ihres Gewichtes ausmachte, was höchstens das spez. Gewicht der 100 % Blausäure schätzungsweise um 5 Einheiten der 4. Decimale und bei verdünnter Blausäure proportional um weniger vermehrt hat. Wir haben dafür keine Korrektion an die beobachteten Werte angebracht.

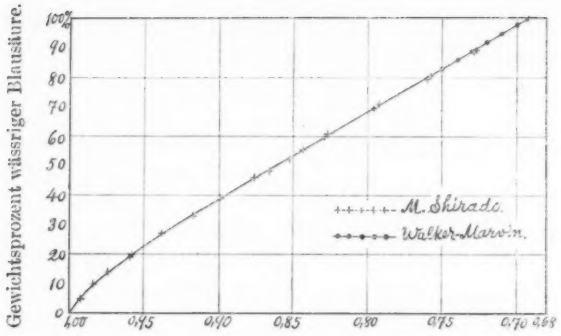


Fig. 1.

funden haben und die reduzierten Werte auf den leeren Raum $D_4^{18.0} = 0.6913$ berechnet haben. Es ist interessant zu erwähnen, dass Walker und Marvin bei 18°C. 0.693 für 99.8 % -ige Blausäure gefunden haben[1] und dass durch Extrapolieren ihrer Werte auf 100 % -ige Blausäure sich 0.692 ergibt. Dieses Resultat stimmt überein mit unseren Werten. Enklaar[2] hat $D_4^{16.4} = 0.6936$ mit einem Temperaturkoeffizienten von 0.0013 gefunden. Aus diesem Werte wird $D_4^{18.0} = 0.6915$ erhalten, während wir aus $D_{18.0}^{18.0}$ den Wert $D_4^{18.0} = 0.6913$ berechnen. Dieses Resultat stimmt gut überein mit unseren Werten.

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THE ACTIVITY OF PHENOL IN AQUEOUS SALT SOLUTIONS[3]

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Received March 2, 1927. Published May 28, 1927.

The fact, that the solubility of non-electrolytes is lowered by the presence of neutral salts, is well known[4] under the term "salt action" or "salting out." For the study of this problem, partition experiments are

(1) M. Walker und C.J. Marvin, loc. cit., **18** (1926), 140.
(2) C.J. Enklaar, loc. cit.
(3) Read before the Chemical Society of Japan, February, 1925.
(4) Rothmund, "Löslichkeit."

often made. In my previous work[1] the molecular states of phenol in benzene and in water were determined by the partition experiments. In the present paper the studies of salt action on phenol will be described.

Partition of Phenol between Benzene and Aqueous Solutions of Neutral Salts. The measurements were carried out at 25°C. in the same manner as described in the previous paper. All the salt used were purifed by recrystallisation. The results are shown in the following tables, where B and C represent the molar concentrations of phenol in the benzene and in the aqueous layer respectively, while S represents the moler concentration of the added salt.

TABLE 1.

Salt	Conc. of salt. mols (S)	Liquids. B=Benzene layer. C=Water layer.	Conc. of phenol. mols.				
NaCl	2.0	B	1.5142	0.7590	0.4383	0.2052	—
		C	0.1282	0.0912	0.0656	0.0379	—
	1.0	B	1.4573	0.7187	0.4126	0.1913	—
		C	0.1851	0.1316	0.0913	0.0518	—
	0.5	B	1.4180	0.6946	0.3948	0.1839	—
		C	0.2244	0.1557	0.1091	0.0593	—
NaBr	2.589	B	0.9316	0.6444	0.4186	—	—
		C	0.0883	0.0738	0.0562	—	—
	1.2945	B	0.8842	0.6077	0.3916	0.1937	—
		C	0.1357	0.1106	0.0832	0.0498	—
	0.6472	B	0.8513	0.5825	0.3734	—	—
		C	0.1686	0.1357	0.1014	—	—
$NaNO_3$	3.0	B	1.1931	0.9045	0.6256	0.2872	0.1399
		C	0.1159	0.1023	0.0827	0.0484	0.0280
	2.0	B	1.1583	0.8756	0.6029	0.2757	0.1334
		C	0.1507	0.1313	0.1050	0.0599	0.0344
	1.0	B	1.0911	0.8205	0.5757	0.2604	0.1257
		C	0.1902	0.1651	0.1326	0.0752	0.0421
	0.5	B	1.0697	0.8025	0.5614	0.2519	0.1225
		C	0.2117	0.1830	0.1469	0.0837	0.0453
	0.25	B	1.0559	0.7907	0.5535	0.2437	0.1198
		C	0.2251	0.1949	0.1547	0.0882	0.0481
Na_2SO_4	1.007	B	1.3138	0.8178	0.6493	0.3419	—
		C	0.1008	0.0820	0.0689	0.0458	—
	0.5166	B	1.1606	0.6111	0.3193	—	—
		C	0.1505	0.1071	0.0684	—	—
	0.2583	B	1.1210	0.5851	0.3812	0.1380	—
		C	0.1901	0.1331	0.1004	0.0451	—
	0.1292	B	1.0978	0.5698	0.3705	0.1342	—
		C	0.2133	0.1484	0.1112	0.0489	—

(1) K. Endo, this journal, **1** (1926), 25.

Salt	Conc. of salt. mols.	Liquids. B = Benzene layer. C = Water layer.	Conc. of phenol. mols.				
KCl	2.0390	B	1.4956	0.7445	0.4302	0.2012	—
		C	0.1468	0.1058	0.0771	0.0419	—
	0.9917	B	1.4399	0.7083	0.4043	0.1887	—
		C	0.2025	0.1420	0.0996	0.0544	—
KBr	2.3533	B	0.8331	0.5215	0.2767	—	—
		C	0.1165	0.0885	0.0568	—	—
	1.1766	B	0.7978	0.4957	0.2597	—	—
		C	0.1518	0.1143	0.0738	—	—
	0.5883	B	0.8372	0.5726	0.3667	0.1804	—
		C	0.1827	0.1457	0.1081	0.0630	—
KNO_3	2.0007	B	1.4505	0.7159	0.4094	0.1910	—
		C	0.1919	0.1344	0.0945	0.0521	—
	0.9989	B	1.4127	0.6897	0.3927	0.1828	—
		C	0.2297	0.1606	0.1112	0.0603	—
K_2SO_4	0.50305	B	1.1489	0.6033	0.3951	0.1442	—
		C	0.1622	0.1149	0.0833	0.0389	—
	0.25136	B	1.2083	0.7396	0.3774	0.1369	—
		C	0.2063	0.1601	0.1043	0.0462	—

The data for NaCl in Table 1 are shown graphically in Fig. 1, which represents three B–C curves (namely $S=2$, $S=1$ and $S=0.5$), in comparison with the theoretical curve of $S=0$ drawn according to the equation[1]

$$B = 2.272C_0 + 37.71C_0^3$$

where C_0 denotes the molar concentration of phenol in the aqueous layer without any salt. As we see in the figure, all the B–C curves deviate leftward from the theoretical curve of $S=0$ and the deviation increases with the amount of the salt added. Obviously this shows the decrease of phenol concentration in the aqueous layer and the increase in the benzene layer by the addition of sodium chloride, that is, salting out. The degree of salting out increases with the increase of the salt concentration. The same can be stated as to other salts. Curves are here omitted.

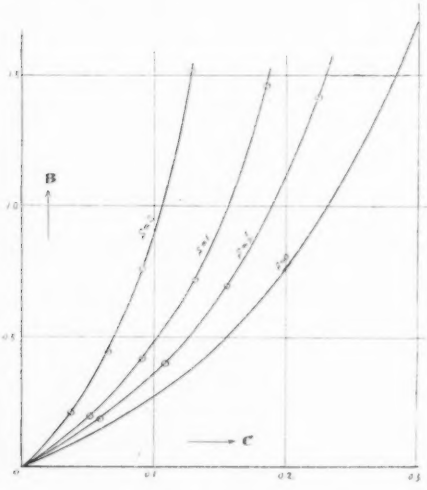

Fig. 1.

(1) Endo, loc. cit.

Thorne[1], studying the solubility of ether in the aqueous solution of sodium chloride, confirmed that the oldest empirical law of Setschenow is valid in his case, namely,

$$\frac{1}{S}\log\frac{\eta_0}{\eta}=k \quad \text{or} \quad \eta=\eta_0 e^{-kS},$$

where η_0 and η denote the solubilities of non-electrolytes in pure water and in aqueous salt solutions respectively, while k is a constant.

Now in the present case, I have also found this logarithmic formula quite valid. For example the case of sodium chloride is shown in Table 2, where the calculations were made with regard to the three horizontal lines (namely $B=1.0$, $B=0.7$ and $B=0.4$) in Fig. 1.

TABLE 2.

S	C	$\log C$	$\log C_0-\log C$	$\frac{1}{S}\log\frac{C_0}{C}=\beta$
		$B=1.0$		
0	$0.2320=C_0$	$\bar{1}.3655$	—	—
0.5	0.1905	$\bar{1}.2799$	0.0856	0.1712
1.0	0.1570	$\bar{1}.1959$	0.1696	0.1696
2.0	0.1060	$\bar{1}.0253$	0.3402	0.1701
		$B=0.7$		
0	$0.1913=C_0$	$\bar{1}.2817$	—	—
0.5	0.1560	$\bar{1}.1931$	0.0886	0.1772
1.0	0.1290	$\bar{1}.1106$	0.1711	0.1711
2.0	0.0870	$\bar{2}.9395$	0.3422	0.1711
		$B=0.4$		
0	$0.1345=C_0$	$\bar{1}.1287$	—	—
0.5	0.1100	$\bar{1}.0414$	0.0873	0.1746
1.0	0.0895	$\bar{2}.9518$	0.1769	0.1769
2.0	0.0612	$\bar{2}.7867$	0.3420	0.1710
		mean $\beta=0.172$		

Thus the constancy of β is satisfactory. Similarly the values of β for other salts are constant. They are shown in Table 3, where their differences are also indicated.

(1) Thorne, *J. Chem. Soc.*, **119** (1921), 262.

TABLE 3.

The values of β and their differences.

Anions / Cations	Cl'	Cl'-NO_3'	NO_3'	Br'-NO_3'	Br'	$\frac{1}{2}SO_4''$-Br'	$\frac{1}{2}SO_4''$
$Na^{\cdot}$	0.172	0.059	0.113	0.042	0.155	0.055	0.210
$Na^{\cdot}$-$K^{\cdot}$	0.039	—	0.033	—	0.044	—	0.039
$K^{\cdot}$	0.133	0.053	0.080	0.031	0.111	0.069	0.180

We see in this table that β is an additive property.

Next we will consider the thermodynamical meanig of this law. Let X represent the chemical potential of phenol in the aqueous salt solution and Z be that quantity for unit concentration. Then

$$X = Z + RT \ln C$$

where T denotes the absolute temperature and R is the gas constant. If these corresponding quantities in the absence of salt are indicated by suffix 0, then

$$X_0 = Z_0 + RT \ln C_0.$$

Along a horizontal line in Fig. 1,

$$X = X_0 = \text{constant},$$

therefore

$$Z - Z_0 = RT(\ln C_0 - \ln C) = RT \ln \frac{C_0}{C}$$

From the above observation

$$\frac{1}{S} \log \frac{C_0}{C} = \beta \quad \text{or} \quad \frac{1}{S} \ln \frac{C_0}{C} = 2.303\,\beta.$$

Hence

$$\frac{Z - Z_0}{S} = \alpha.$$

where $\alpha = 2.303\,\beta RT$, which is constant for a constant temperature.

Thus the elevation of the chemical potential of phenol for unit concentration by the addition of a neutral salt is proportional to the salt concentration.

Now we can obtain the equation of B-C curves in Fig. 1. As indicated already,

$$B = 2.272\,C_0 + 37.71\,C_0^3,$$

while

$$\log \frac{C_0}{C} = \beta S \quad \text{or} \quad C_0 = 10^{\beta S} C.$$

Therefore

$$B = 2.272 \times 10^{\beta S} C + 37.71 \times 10^{3\beta S} C^3 \quad \cdots\cdots\cdots\cdots\cdots\cdots (1)$$

This equation (1) is found quite valid. For example, the case of $NaNO_3$ is shown in Fig. 2, where the curves have been drawn according to the equation (1) and the observed points are denoted by circlets.

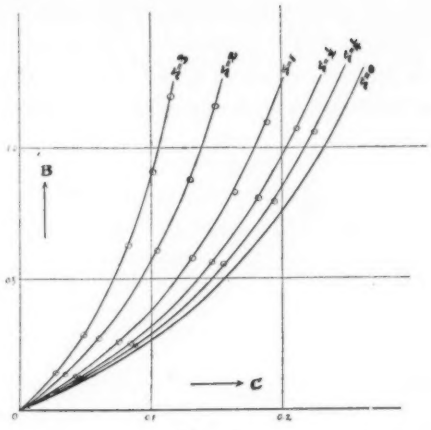

Fig. 2.

The Effect of Sodium Nitrate on the Depression of Freezing Point of Aqueous Phenol Solution. In the first place, the measurements on the depression of freezing point of the aqueous solution of sodium nitrate alone were made in the same manner as described in my previous paper, although on this same topic there are sevaral previous reports of experiments which are sometimes not accurate. The results are shown in Table 4, whereafter the molar concentrations are calculeted in mol per 1000 grams of water.

TABLE 4.

Depression of freezing point of the aqueous solution of $NaNO_3$.

Water gr.	$NaNO_3$ gr.	Molar concentrations of $NaNO_3$ S	Depressions of freez. pt. by $NaNO_3$ in degree. Ds.
499.4	2.3105	0.0542	0.189
499.4	4.6406	0.1093	0.373
499.4	8.5151	0.2006	0.670

In the next place, the cryoscopic measurements of the aqueous solution of both phenol and sodium nitrate were made, the result of which are shown in Table 5.

TABLE 5.

Depression of freezing point when both phenol and $NaNO_3$ are simultaneously dissolved in water.

Water gr.	Phenol gr.	Molar conc. of phenol (C)	$NaNO_3$ gr.	Molar conc. of $NaNO_3$ (S)	Depression of freez. pt. in degree. D_{P+S}
499.5	10.198	0.217	0.	0.	$0.388 = D_P$
499.5	10.198	0.217	3.7495	0.0883	0.695
499.5	10.198	0.217	6.9650	0.1640	0.952
499.5	10.198	0.217	9.9715	0.2348	1.185

Subtracting the depression of phenol alone (D_P), from that by the combination of the two solutes (D_{P+S}) in Table 5, the depression apparently due to sodium nitrate is obtained as shown in Table 6, provided that the depression is the additive property of solutes.

TABLE 6.

Portions of depression apparently due to $NaNO_3$ when $C=0.217$.

S	$D_{P+S}-D_P$
0	0
0.0883	0.307
0.1640	0.564
0.2348	0.794

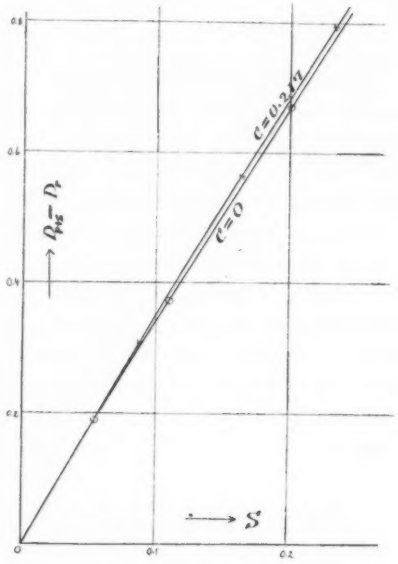

Fig. 3.

These depressions in Table 6 and those in Table 5, which are really due to sodium nitrate, are compared graphically in Fig. 3.

If the additivity holds in this case as assumed, the two curves must coincide, but we see a small discrepancy in the concentrated part. In the first section of this paper, I reached the conclusion that the chemical potential of phenol can be expressed in the following formula,

$$X = Z_0 + \alpha S + RT \ln C$$

or

$$X = Z_0 + RT \ln \left(e^{-\frac{\alpha}{TR}S} C \right).$$

Now, as $e^{-\frac{\alpha}{RT}S}$ is so-called "activity coefficient," the activity of phenol and consequently, the depression of freezing point due to phenol must increase when a salt is added (that is, $S>0$). And so the above discrepancy of the curves should become perceptible when S is sufficiently great. Actually the curve $C=0.217$ deviates upwards from the curve $C=0$ and the deviation gradually increases with the concentration of sodium nitrate. Therefore, Fig. 3 offers a qualitative proof for the above equation obtained from the study of partition.

However, when the concentration of salt is small, owing to the small value of $\frac{a}{RT}$, the activity coefficient is nearly equal to unity and the effect of salt is negligible. That is why we cannot perceive the discrepancy at the dilute part in Fig. 3.

Summary.

1. From the measurements on the partition of phenol between benzene and the aqueous solutions of neutral salts, it has been found that the following logarithmic law practically holds,

$$\frac{1}{S}\log\frac{C_0}{C}=\beta$$

Applying this to the equation of the chemical potential of phenol it becomes

$$\frac{Z-Z_1}{S}=a.$$

We have also obtained an equation of phenol distribution between benzene and water in the presence of neutral salts at 25°C:

$$B=2.272\times10^{\beta S}C+37.71\times10^{3\beta S}C^3.$$

2. From the measurements of the freezing points of the aqueous phenol solutions in the presence of a neutral salt, it has qualitatively been proved that the chemical potential of phenol can be expressed in the following formula,

$$X=Z_0+aS+RT\ln C$$

and the activity coefficient of phenol is, therefore, to be expressed as

$$e^{-\frac{a}{RT}S}.$$

The author's thanks are due to Prof. K. Ikeda for his kind guidance in the present investigation.

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THE DENSITIES OF MAGNESIUM AT ITS MELTING POINT.

By **Hikozô ENDO.**

Received March 30, 1927. Published May 28, 1927.

Introduction. Most of the well-defined properties of elements change periodically when they are arranged in order of their atomic weight, for example, atomic volume, specific gravity, melting point, magnetic susceptibility, electric and thermal conductivities, compressibility, arc spectra etc.

When the numerical values are plotted against the atomic weights, the curve obtained is broken up into periods, the shape of period varying according to the property tabulated.

The present writer[1] also stated the periodicity of the change of volume of elements on melting to their atomic weights as illustrated in Fig. 1.

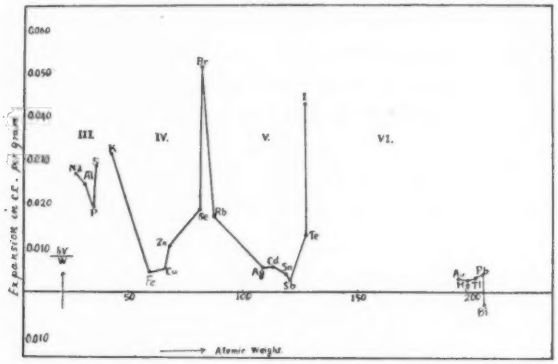

Fig. 1.

The first period in the curve corresponds to the third series of the Mendelejeff's periodic table. A complete short period contains eight elements and a complete long period, eighteen, which are made up of series connected by a transition groups of three elements. Within any one period, whether short or long, there is no sudden change in chemical and physical properties in general as we pass from one element to the next in order. But when we pass from one period to the next, there is a sudden change in the properties of consecutive elements. These sudden changes in the properties correspond in Fig. 1 to sudden change in the direction of the curves. In the Mendelejeff's table, the elements which are located near one another have general resemblance in their properties. From Fig. 1, therefore, it is highly probable that the amount of volume change on melting per unit mass of magnesium will intermediate between those of sodium and aluminium. The volume change on melting per one gram of sodium is 0.0243 c.c. and that of aluminium 0.0267 c.c., hence that of magnesium will be about 0.0255 c.c.

The value of volume change can be obtained if we were able to measure the densities of magnesium at its melting point both in the solid and the liquid states. But the density of magnesium at high temperature has not

(1) H. Endo: *Sci. Rep. Tohoku Imp. Univ.*, **13** (1924), 193; The eighty-eighth report of the Research Institute for Iron, Steel and Other Metals.

yet been determined. So the author has calculated the densities of magnesium at its melting point under the assumption that the above value of the volume change is reasonable.

Experimental. The density of solid at its melting point might easily be calculated from the mean coefficient of cubical expansion of magnesium from room temperature to the vicinity of its melting point. The mean coefficient of linear expansion of the metal has been measured accurately with the dilatometer constantly used in our Institute.[1] The measurement was always made in a vacuum high enough to avoid the oxidation of the specimen. The rate of heating was slow, the whole time required for heating the specimen from room temperature to 600°C. extending over three hours. From the observed data, the elongation $\partial l/l$ of the specimen, whose length is l, was calculated. The mean coefficients of linear expansion of magnesium at various temperatures measured with the apparatus are illustrated in Fig. 2.

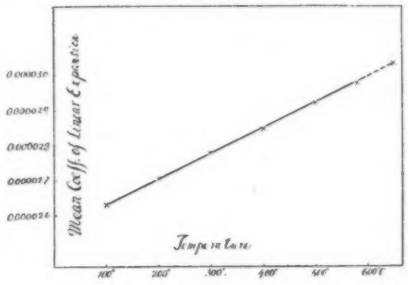

Fig. 2.

The melting point of the metal is 650°C. and, therefore, the mean coefficient of expansion between 20°C. and 650°C. can be deduced by extraporation, thus it has been known to be 0.00003025. Then the mean coefficient of cubical expansion will be calculated as follows:—

$$\beta = 3\alpha = 0.00003025 \times 3 = 0.00009075.$$

The specific volume of the solid state of magnesium at its melting point is 0.60724 c.c. that is:

$$V_s = V_{20}(1+\beta t) = 0.5744(1+0.00009075 \times 630) = 0.60724$$

where V_{20} is the specific volume of the metal at 20°C. The density of the solid state at the melting point is reciprocal of the specific volume that is:—

$$\rho_s = \frac{1}{V_s} = \frac{1}{0.60724} = 1.6468$$

The Density of Magnesium in Liquid State at its Melting Point. The density of the liquid state of the metal at its melting point can easily be calculated from the density of solid state and the amount of the change of volume per unit mass on melting which described above. The writer published the results of measurements of the change of volume in several

(1) *Sci. Rep. Tohoku Imp. Univ.*, 6 (1917), 203.

metals and alloys during solidification with a thermo-balance.[1] The result was that, with the exception of bismuth and antimony, all of the metals and alloys studied show the contraction during solidification. Therefore it may reasonably be assumed that the magnesium also expands during melting, and the amount of it is 0.0255 c.c. per gr. which was derived from the periodic curve described above.

Then the specific volume of the liquid state of magnesium at its melting point is,

$$V_l = 0.60724 + 0.0255 = 0.63274 \text{ c.c.}$$

And the density of the liquid magnesium at its melting point is,

$$\rho_l = \frac{1}{V_l} = \frac{1}{0.63274} = 1.5804.$$

The mean coefficients of linear expansions at several temperatures which have been obtained by measurements are tabulated in the following table.

Temp. C.	Mean linear exp. coeff.	Temp. C.	Mean linear exp. coeff.
20~100	0.0000263	20~500	0.0000292
20~200	0.0000271	20~580	0.0000299
20~300	0.0000278	20~650	0.0000303
20~400	0.0000284		

Density of solid magnesium at 20°C = 1.7410
Density of solid at melting point = 1.6468
Density of liquid at melting point = 1.5804.

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ON THE PRESERVATION OF THE STANDARD SOLUTION OF OXALIC ACID AND ON THE READING OF THE BURETTE.[2]

By **Saburo ISHIMARU.**

Received April 6, 1927. Published May 28, 1927.

As is generally known, the solution of oxalic acid is widely used as an important standard in volumetric analysis, though it is necessary to prepare it frequently anew on account of its tendency to decomposition, but

(1) K. Honda, *Sci. Rep. Tohoku Imp. Univ.*, 4 (1915), 97.

(2) This paper was published in Japanese in the *Journal of the Chemical Society of Japan*, 43 (1922), 767.

very few books on analytical chemistry describe the method of preservation of this solution.

The addition of alcohol was formerly proposed by Hartly[1] and thymol by Gerland[2] as preserving agents. Riegler[3] on the other hand, described that a solution containing 50 c.c. of conc. sulphuric acid in 1 litre did not alter its titre after a year. Treadwell[4] recommended the same precaution in his famous book of analytical chemistry, and advised not to use old solutions prepared in the usual manner without any preserving agent, on the basis of his observation that an oxalic acid solution prepared according to the method of Riegler lost, after eight months' standing, only 0.07% of its original strength, while one containing no sulphuric acid lost 0.57%.

Werner[5] and Blass[6] attributed the cause of the decomposition of oxalic acid to the action of a micro-organism, Bizio,[7] Fleury[8] and Gigli[9] expressed the opinion that the concentrated solutions were not subject to the influence of the harmful micro-organism and Duclaux[10] and Jorissen[11] described about the action of light upon it.

As the degree of the deterioration observed by Treadwell and Riegler in the oxalic acid solution containing sulphuric acid was too small to be in accordance with the author's experience, it was suspected that there might have been something wrong with their observations. The author also wondered why the two investigators had used so large a quantity of conc. sulphuric acid as 50 cc. for the purpose of preservation, though as a matter of course, a small quantity of it must have exerted a sufficiently disinfecting effect.

The experiments to be here described were carried out by the present author, in order to clear up the points in question, by a thoroughly systematical investigation, with the view that the most important of the influential factors as regards the preservation of the standard oxalic acid solution would probably be the action of light.

Two series of 0.1 N solutions of oxalic acid, with and without the addition of the various quantities of conc. sulphuric acid were prepared from

(1) *Chem. News*, **37** (1878), 9.
(2) *J. Soc. Chem. Ind.*, **10** (1891), 25.
(3) *Z. analyt. Chem.*, **35** (1896), 522.
(4) „Lehrbuch der analytischen Chemie," 7th ed. II, p. 499.
(5) *Arch. Pharm.*, [3], **2** (1873), 522.
(6) Ibid., [3], **3** (1873), 310.
(7) *Z. analyt. Chem.*, **9** (1870), 392.
(8) *J. pharm. chim.*, [5], **7** (1883), 383; *Chem. Zentr.*, (1883), 547.
(9) *Apoth. Zt.*, **7** 583; *Chem. Zentr.*, (1893), I, 11.
(10) *Comp. rend.*, **103** (1886), 1010.
(11) *Z. angew. Chem.*, (1899), 521.

Kahlbaum's purest oxalic acid ("Zur Analyse"): the one series was kept in ordinary colorless reagent bottles, while the other, in reagent bottles completely wrapped with black paper.

For the sake of studying the disparity, if any, between the degrees of the deterioration of the solutions differing in purity, the duplicates of the whole series were made from oxalic acid of the pure commercial grade.

All the bottles were kept in rows, on the laboratory shelves, which were beyond the reach of the *direct* sun light. From time to time, the rate of decomposition was measured, by titration with a standard solution of potassium permanganate, standardized against the pure oxalic acid solution, *freshly* prepared each time from Kahlbaum's preparation ("Zur Analyse").

In order not to exclude the chance of development of the micro-organism, the investigation was begun in April and continued till September; the reagent bottles were simply closed with glass stoppers applying neither special sealing nor sterilization, so that the conditions would be kept the same, as far as possible, with those prevailing in the ordinary analytical practice.

TABLE 1.

(Oxalic acid: Kahlbaum, "Zur Analyse." Containers: ordinary colorless reagent bottles.)

No. of experiment.	Conc. H_2SO_4 in L. cc.	Normality.				
		1st day.	47th day.	90th day.	148th day.	Difference.
1	0	0.0991	0.0991	0.0991	0.0987	−0.0004
2	2	0.0992	0.0990	0.0986	0.0981	−0.0011
3	10	0.0990	0.0983	0.0980	0.0951	−0.0039
4	20	0.0992	0.0972	0.0941	0.0900	−0.0092
5	40	0.0992	0.0965	0.0929	0.0890	−0.0102
6	100	0.0992	0.0941	0.0887	0.0827	−0.0165

TABLE 2.

(Oxalic acid: commercial. Containers: ordinary colorless reagent bottles.)

No. of experiment.	Conc. H_2SO_4 in L. cc.	Normality.				
		1st day.	48th day.	91st day.	149th day.	Difference.
7	0	0.0993	0.0993	0.0986	0.0982	−0.0011
8	2	0.0993	0.0987	0.0980	0.0975	−0.0018
9	10	0.0993	0.0985	0.0970	0.0955	−0.0038
10	20	0.0993	0.0978	0.0960	0.0943	−0.0050
11	40	0.0990	0.0970	0.0938	0.0908	−0.0082
12	100	0.0991	0.0960	0.0927	0.0899	−0.0092

From the figures given in Tables 1 and 2, it is clearly shown that, contrary to the general belief now prevailing among chemists, the plain aqueous solutions are comparatively most stable (Nos. 1 and 7), and the solutions become more and more unstable as the quantities of sulphuric acid added are increased (No. 12 lost more than 9%, while No. 6 even 16% or so, of the original strength). Accordingly the method, recommended by Treadwell and Riegler, of adding sulphuric acid to the standard solution of oxalic acid and keeping it in the ordinary *colorless* bottle, is altogether of no practical value as a means of preservation.

It will also be seen that in the presence of fairly large quantities of sulphuric acid, the solutions of Kahlbaum's purest oxalic acid (Nos. 4–6) are less stable than those of the pure commercial sample (Nos. 10–12).

TABLE 3.

(Oxalic acid: Kahlbaum, "Zur Analyse." Containers: reagent bottles wrapped with black paper.)

No. of experiment.	Conc. H_2SO_4 in L. cc.	Normality.				
		1st day.	47th day.	90th day.	148th day.	Difference.
13	0	0.0992	0.0992	0.0992	0.0992	0.0000
14	2	0.0990	0.0992	0.0990	0.0992	+0.0002
15	10	0.0992	0.0992	0.0991	0.0995	+0.0003
16	20	0.0990	0.0992	0.0991	0.0995	+0.0005
17	40	0.0992	0.0992	0.0992	0.0995	+0.0003
18	100	0.0994	0.0992	0.0992	0.0993	−0.0001

TABLE 4.

(Oxalic acid: commercial. Containers: reagent bottles wrapped with black paper.)

No. of experiment.	Conc. H_2SO_4 in L. cc.	Normality.				
		1st day.	48th day.	91st day.	149th day.	Difference.
19	0	0.0993	0.0992	0.0992	0.0994	+0.0001
20	2	0.0991	0.0993	0.0992	0.0995	+0.0004
21	10	0.0991	0.0992	0.0992	0.0995	+0.0004
22	20	0.0993	0.0992	0.0992	0.0994	+0.0001
23	40	0.0991	0.0992	0.0991	0.0995	+0.0004
24	100	0.0993	0.0993	0.0991	0.0996	+0.0003

The results given in Tables 3 and 4 indicate, that the plain aqueous solutions of oxalic acid, kept in the bottles completely wrapped with black paper, without any precaution for excluding the influence of the micro-

organism, are all strikingly stable, entirely regardless of the difference in the grades of purity of the materials (Nos. 13 and 19); even those containing large quantities of sulphuric acid are also stable when kept in the *black* bottles (Nos. 18 and 24).

The negligible increase, observed in the concentrations of these solutions, must naturally be explained to be due partly to the experimental error and partly to the slight evaporation during the extreme heat in the summer. Had the bottles, with specially well ground and perfectly fitted stoppers, instead of the *ordinary* reagent bottles, been used in the above experiment for keeping the solutions, the concentrations would doubtless have remained absolutely the same.

From the results stated thus far, it is clearly established, that the standard solution of oxalic acid should always be kept in a bottle carefully wrapped with black paper, and that the addition of sulphuric acid is entirely unnecessary.

What then was the reason which led Treadwell and Riegler to such an erroneous conclusion? It seems very plausible, in the light of the author's observation recorded above, that the two investigators accidentally kept their solutions for the experiments of preservation, in a more or less dark place—most probably inside the laboratory table.

On the Reading of the Burette.

For the purpose of making the reading of the burette easy and accurate, there have been many devices proposed, such as the use of a mirror, etc., but none of them satisfies the following five conditions at the same time, namely, (1) constancy of the background of the meniscus, (2) deep coloration of the meniscus, (3) facility of fixing the position of the experimenter's eye, (4) easy and comfortable reading of the graduations of the burette, none of them being covered from sight, and lastly (5) no necessity of holding it by hand.

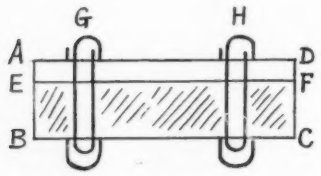

Fig. 1.

The device to be here described, is the one constantly used by numerous workers, in this laboratory of analytical chemistry for several years and found to answer all the requirements enumerated above.

A piece of paper ABCD, measuring 22 cm. × 8 cm., is cut from a name card, as shown in the accompanying figure, on which is pasted a strip of black glazed paper EBCF, measuring 1.5 cm. × 8 cm.: then a strip of transparent colorless celluloid plate, having exactly the same size as the glazed

paper EBCF, is fastened by two paper clips, G and H, to the card, so that the edges of the glazed paper and celluloid perfectly coincide on the line EF, between which the burette is inserted. When it is moved until the meniscus seems to touch the line EF, the afore-mentioned conditions are satisfied simultaneously and the reading is made exceedingly easy and accurate.

Summary.

(1). The standard solution of oxalic acid should always be kept in a reagent bottle carefully *wrapped with black paper.* The solution thus preserved does not change its strength, irrespective of the presence or absence of sulphuric acid. Hence the old standard solution kept in a black bottle can as well used for titration.

(2). The method of preservation of the oxalic acid solution, described in Treadwell's "Analytical Chemistry" is not appropriate; the addition of sulphuric acid is not only unnecessary but *objectionable,* because the velocity of decomposition of the oxalic acid solution kept in a *colorless* bottle, becomes greater with the increase in the concentration of sulphuric acid added.

(3). A convenient device for the correct reading of the burette is described.

In conclusion, the author wishes to express his heartfelt thanks to Prof. M. Kobayashi for valuable suggestions during the work.

September, 1922.

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ÜBER DIE DICHTE VON SYSTEM DES NIKOTIN-WASSERS.

Von **Naoyasu SATA.**

Eingegangen am 10. April 1927. Ausgegeben am 28. Mai 1927.

Einleitung. Das abnorme Verhalten des Systems von Nikotin-Wassers nämlich betreffend ihre Lösungskurve wohl bekannt ist und besonders durch frühere Beobachtung von Hudson[1] und die spätere von Tsakalotos[2]. Die beiden beobachtete in diesem Falle noch interessante Frscheinung, dass

(1) *Z. physik. Chem.*, **47** (1904), 113.

(2) *Bull. soc. chim.*, **5** (1909), 397; Z. physik. Chem., 60 (1907), 567; *J. Chem. Soc.*, **115** (1919), 104; Bakhuis Roozeboom, „Heterogenen Gleichgewichte," 2 Heft, 2 Teil (Systeme mit zwei flüssigen Phasen, von E.H. Büchner), Braunschweig, 1918.

dieses über ca. 60°C. in zwei flüssigen phasen getrennte System bei ca. 90°C. der Platzwechsel der beiden Phasen geschiet während es über 210°C. sich wieder zu homogener System mischt. Wenn es tatsächlich der Fall ist, und anstatt der Lösungskurve mit der Dichte-Temperaturkurve gezeichnet wird, so sollte es zwischen 60°C. und 210°C. S-artig werden und deren Kleuzpunkt soll mit dem Platzwechselpunkt übereinstimmen.

Um das genannte Verhalten betreffend die Dichtemessung bei der gleichmässig hohen Temperatur (näher und über den Siedepunkt der Flüssigkeit) durch eine experimentele Untersuchung graphisch darzustellen, nahm ich die vorliegend Arbeit vor.

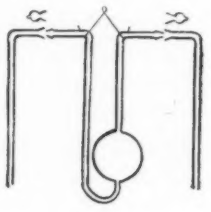

Fig. 1.

Versuchsmethoden. *Pyknometer:* Von 30°C. bis 95°C. gebraucht ich gewöhnlichen Pyknometer von Sprengelschem Rohr, mit geschliffenem Stöpsel und Einleitungsrohr (Fig. 1). Über 100°C., also das Wasser wird siedende Hitze, müssen wir Apparat mit eigentümlicher Einrichtung gebrauchen wie Fig. 2.

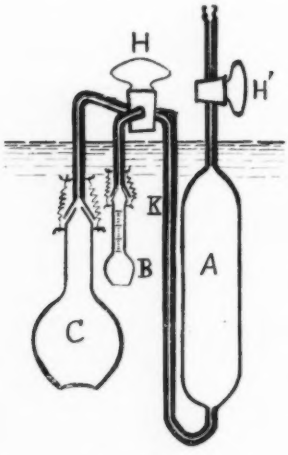

Fig. 2.

A: Gleichgewichtsgefäss.
B: Pyknometer.
C: Reservoir.
H: Dreiweghahn.
H′: Hahn.

Anwendungsmessmethode, wie folgt: Erstens evakuiert man A, B und C durch H, H′ mit dem Pumpen, hier schliesst man Dreiweghahn H, dann leitet Nikotin-Wasser Gemisch im Gleichgewichtsgefäss A ein, taucht man ganzen Apparat im Thermostat, wiederholt geschüttert bis das System das Gleichgewicht erreicht. (Es erkannt mit der klaren Aufscheidung der zwei flüssigen Phasen.)

Hier öffnet man Dreiweghahn H zum C, gibt die nichtgleichgewichte Teile in Kapillarrohr K in C auf, dann H zum B öffnet, füllt Pyknometer B ein, Skalen des Pykometerhalses lese und wäge.

Für Messungen oberer Phasen, gibt man ganze Unterphase in das Reservoir auf und säugt im Pyknometer obere Phase allein.

Thermostat: Unter 100°C., gewöhnlichem Wesserbade ist es gebräuchlich, nur aber ihre Oberfläche mit Paraffinöl bedeckt um Verdampfung des

Wassers zu verhindern. Über 100°C. benutzte ich Paraffinölbade mit elektrischer Heitzung und Temperaturregulierung, wie bei Dr. Shirai.[1]

Materien. *Nikotin:* Kahrbaum Präparate wird gebraucht. Durch Destillation unter vermindertem Druck in einem Wasserstoffstrome erhalten wir ganz farblose Flüssigkeit, aber es färbt sich bräunlich trotz der Aufbewahrung im Exikator im Dunkel. Deswegen am Anfang jeder Versuchen musste wieder destilliert werden.

Wasser: Man verwendet destilliertes Wasser mit genügendem Sieden, um gelöste Kohlensäure etc. zutreiben.

Versuchsresultaten. 1-*Versuchsreihe:* Dichte des Nikotin-Wasser Gemisches jedes Vol. % zwischen 30°C. und 60°C. gemessen.

Tabelle 1.

°C / vol.% Nikotins	30	40	50	60
0	0.99567	0.99225	0.98807	0.98324*
10	1.00234	1.99856	0.99453	0.98968
20	1.00888	1.00410	0.99886	0.99353
30	1.01513	1.00953	1.00381	0.99755
40	1.02118	1.01449	1.00784	1.00065
50	1.02646	1.01903	1.01033	1.00299
60	1.03023	1.02156	1.01280	1.00407
70	1.03101	1.02228	1.01247	1.00406
80	1.02788	1.01830	1.00875	0.99979
90	1.01773	1.00979	1.00132	0.99280
100	1.00124	0.99383	0.98630	0.97890

* Landolt Tabellen.

Dieser wurde graphisch wie Fig. 3 dargestellt.

2-*Versuchsreihe:* Jeder Gemisch wird zwischen 60°C. und 65°C. in zwei flüssigen Phasen getrennt. Da über diese Temperatur die Gemische in zwei flüssigen Phasen im Gleichgewicht sich vorfindet, so ist eines mit Wasser gesättigte Nikotin Phase und anders mit Nikotin gesättigte Wasser Phase. Im folgendern sind die Dichte jeder Phasen bei jeder Temperaturen im Gleichgewicht dargestellt.

(1) Diese Zeitschrift, **2** (1927), 38.

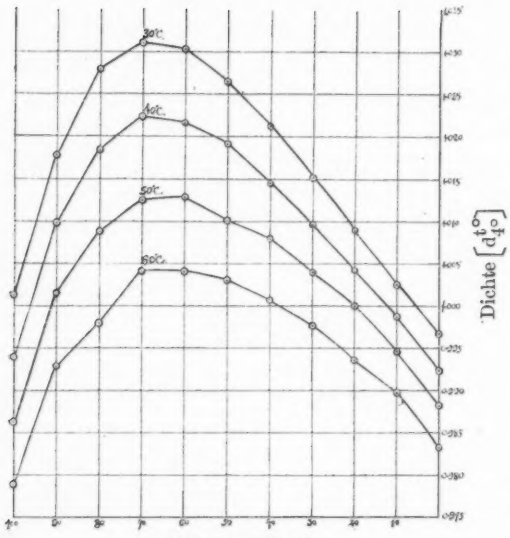

Fig. 3.

Tabelle 2.

°C.	Obere Phase. (mit Nikotin gesättigte Wasser-schicht.)	Untere Phase. (mit Wasser gesättigte Nikotin-schicht.)
65	0.98918	0.99907
70	0.98467	0.99491
75	0.98077	0.98904
80	0.97761	0.98438
85	0.97397	0.97832
90	0.97103	0.97368
95	0.96709	0.96744

3-*Versuchsreihe:* In dieser Reihe wurde genau ebenso wie in 2-Versuchsreihe die Dichte beiden Phasen von 100°C. bis 120°C. gemessen nur aber im Gebrauche von genanntem eigentümlichem Apparat, wegen des Über-Siedepunkt des Wassers.

Tabelle 3.

°C.	Untere Phase. (mit Nikotin gesättigte Wasser-schicht.)	Obere Phase. (mit Wasser gesättigte Nikotin-schicht.)
100	0.96420	0.9619
105	0.9607	0.9576
110	0.9571	0.9521
115	0.9534	0.9477
120	0.9497	0.9432

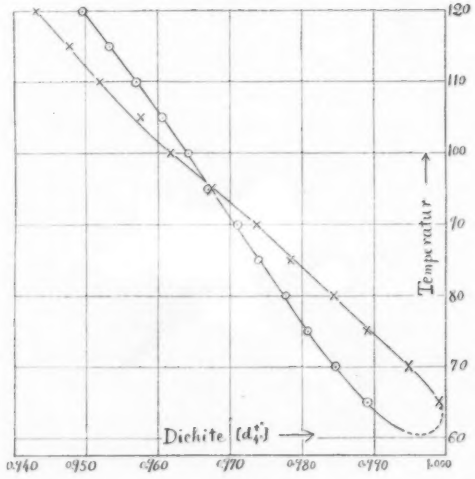

Fig. 4.

Tabelle 2 und 3 wird graphisch wie Fig. 4 dargestellt

Zusammenfassung.

1. Die Dichte der Nikotin-Wasser Gemischen wurden in der Temperaturbereich von 30°C. bis 120°C. gemessen.

2. Vor Trennung in zwei Phasen, nämlich zwischen 30°C. und 60°C. (Fig. 3) Dichte-Vol. % Kurven haben ein Maximum, derer Krümmungen mit der Temperaturerhöhung grösser werden, und zeigen, dass nach der Trennung in zwei Phasen konstante Dichte haben, unabhängig von Verhältnisgehalt der Komponente.

3. Dichte-Temperatur Kurve nach der Trennung in zwei flüssigen Phasen wurde wie 8–artig übergezeugt. (Fig. 4)

4. Beim Kreuzpunkt der Kurve (Fig. 4) müssen die beiden Phasen ganz gleiche Dichte haben und muss der Platzwechsel beider Phasen, deswegen hier geschehen, deren Temperatur als 96°C. nach der Fig. 4 bestimmt wird.

Die vorliegende Arbeit wurde unter Leitung von meinem hochverehrten Lehrer Herrn Prof. J. Sameshima ausgeführt, welchem ich für seine froundliche Anregung und Unterstützung dabei zu herzlichem Dank verpflichtet bin.

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ON W. A. NOYES' METHOD OF PREPARING ETHYL CYANACETATE.

By **Yoshiyuki URUSHIBARA.**

Received April 4, 1927. Published May 28, 1927.

L. Vanino describes in his "Präparative Chemie" W. A. Noyes' method for the preparation of ethyl cyanacetate.[1] But the condensation of the ester prepared by this method and triethyl ortho-formate by means of acetic anhydride[2] produced a substance which on analysis gave such numbers as if it were the *methyl* ethoxy-methylene-cyanacetate $CH_3OCO-C(=CHOC_2H_5)-CN$, the condensation product of methyl cyanacetate and triethyl ortho-formate.[3]

(1) Original note: *J. Am. Chem. Soc.*, **26** (1904), 1545.

(2) In a manner similar to that described by E. Gregoire de Bellemont, *Bull. Soc. Chim.*, [3], **25** (1901), 18.

(3) *Bull. soc. chim.*, [3], **25** (1901), 21.

	C_2H_5OCO-C (=$CHOC_2H_5$)-CN	CH_3OCO-C (=$CHOC_2H_5$)-CN	Fonnd		
			I	II	III
C	56.77	54.19	54.72	55.21	—
H	6.56	5.81	5.93	6.04	—
N	8.28	9.03	—	—	9.22

Thus it is very probable that this cyanacetic ester contained methyl cyanacetate. This can be easily understood if we consider that the ester was prepared by boiling ethyl chloracetate and potassium cyanide in methyl alcohol. Some of the ethyl group of the ester was replaced by the methyl group of the methyl alcohol, which has been ascertained by the following analysis and measurement of density.

A precise determination of nitrogen content of the cyanacetic ester in question showed that this preparation contained about equal parts of ethyl and methyl esters.

	$CNCH_2CO_2CH_3$	$CNCH_2CO_2C_2H_5$	Found		
			I	II	III
N	14.14	12.39	13.32	13.26	13.28

Methyl cyanacetate was prepared from methyl chloracetate by using methyl alcohol as the solvent.(1)

D_4^{17} of methyl cyanacetate = 1.133

D_4^{17} of the ester prepd. by Noyes' method = 1.114

The real ethyl cyanacetate was prepared from ethyl chloracetate by the action of potassium cyanide in absolute ethyl alcohol.(2)

Potassium cyanide is difficultly soluble in ethyl alcohol, while soluble in methyl alcohol, but the yield of cyanacetic ester is scarcely diminished by replacing methyl alcohol by ethyl alcohol.

D_4^{20} of the ester prepd. by Noyes' method = 1.110

D_4^{20} of ethyl cyanacetate = 1.063

The investigation on the diethyl dicyanoglutaconate, the details of which were given in the previous paper,(3) always started from the cyanacetic ester prepared by Noyes' method. In all cases only the ethyl compound, e.i. diethyl sodio-dicyanoglutaconate, was obtained, the yield being sometimes over 60 % of the theoretical amount. Hence we must consider that the

(1) and (2). These esters were fractionated two times under diminished pressure and sufficiently pure for synthetical purposes, but probably not for a precise determination of a physical constant.

(3) This Journal, 2 (1927), 26.

methyl ester contained in the ester mixture was again converted into ethyl ester, for the reaction giving diethyl sodio-dicyanoglutaconate was always carried out in ethyl alcohol. As long as the ester prepared by Noyes' method is used in ethyl alcohol, the absurdity of this method cannot be suspected. It can be foreseen that the ester mixture must give the *dimethyl* sodio-dicyanoglutaconate when it reacts with chloroform and sodium methylate in methyl alcohol. This compound, e.i. dimethyl sodio-dicyanoglutaconate had not been known, but was easily synthesised by using methyl cyanacetate in methyl alcohol.[1] The ester mixture prepared by Noyes' method also gave the same dimethyl sodio-dicyanoglutaconate when it was treated with chloroform and sodium methylate in methyl alcohol. J. C. Hessler and R. M. Lamb[2] observed that they obtained *methyl* esters of alkylcyanacetic acids by alkylation of ethyl cyanacetate in methyl alcoholic solution, but when one experiment was carried out on the alkylation of methyl cyanacetate in ethyl alcohol, the products remained methyl esters. But in the present case the replacement of the alcohol group of the cyanacetic ester seems to be reversible.

$$CNCH_2CO_2CH_3 + C_2H_5OH \gtrless CNCH_2CO_2C_2H_5 + CH_3OH.$$

It is also not impossible that the replacement may occur in the reaction product rather than the cyanacetic ester, and a little amount of water or any other substance may act as a catalyser.

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(1) The details will be given in another paper.
(2) *J. Am. Chem. Soc.* 43 (1921), 205.